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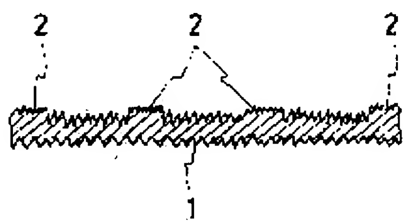
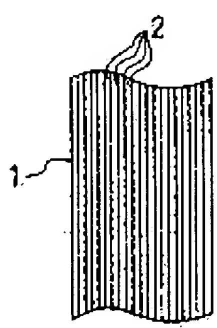
(54) ETCHING METHOD OF ALUMINUM FOIL





(57)Abstract:
PURPOSE: To easily obtain an etched foil excellent in mechanical strength without reducing its surface-enlarging magnification, by performing the treatment of etching an Al foil useful as the electrode of a capacitor while applying many fine lines onto the surface of said foil.
CONSTITUTION: Many fine lines 2 resistant to corrosion are applied onto the surface of an Al foil in parallel with each other, for instance, along the logitudinal, i.e. rolling, direction of the foil 1, and the etching treatment is performed under this condition. Hence, an etched surface having many deep rugged parts where a dissolution amount is large is formed on the surface part onto which the lines 2 are not applied, while an etched surface having many shallow rugged parts where either dissolution is not brought about or a dissolution amount is small is formed on the part onto which the lines 2 are applied. By this constitution, tensile strength along the rolling direction of the foil and bending strength along a direction perpendicular to said rolling direction are made large.

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(54) Title of the invention: Etching Method for Aluminum Foil

(21) Application Number: S57-192390

(22) Date of application: November 4, 1982

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Specification

1. Title of the invention: Etching method for aluminum foil

2. Scope of patent claims:

(1) An etching method for aluminum foil characterized by conducting etching treatment after providing numerous corrosion-resistant fine lines on the aluminum foil surface.

(2) An etching method for aluminum foil according to Scope of patent claim 1 characterized by providing the fine lines in parallel in the rolling direction of the aluminum foil.

(3) An etching method for aluminum foil according to Scope of patent claim 1 characterized by providing the fine lines in slanted form in the rolling direction of the aluminum foil.

(4) An etching method for aluminum foil according to Scope of patent claims 1, 2, or 3 characterized by providing the fine lines on one side of the aluminum foil.

(5) An etching method for aluminum foil according to Scope of patent claims 1, 2, or 3 characterized by providing the fine lines on both sides of the aluminum foil.

3. Detailed explanation of the invention:

This patent application relates to an etching method for aluminum foil that seeks to obtain etching foil that has superior tensile strength and bending strength, and that can avoid damage such as cutting in the winding process of the capacitor element.

As is generally known, aluminum foil that is used in the electrodes of electrolytic capacitors undergoes etching treatment that corrodes the surface in order to increase the effective surface gain.

After conducting etching treatment, however, the mechanical strength such as tensile strength and bending strength of the aluminum foil is reduced by the corrosion. Consequently, in cases where the capacitor element undergoes winding by an automatic winder or the like, there occur troublesome problems such as cutting or the like in the attachment part or wind core part of the terminal. Etching method researchers are currently struggling with regard to how to obtain a large effective surface gain without impairing the mechanical strength of the aluminum foil.

In light of this point, the inventor of the current patent application has done research and succeeded in creating an etching method that easily obtains aluminum foil with superior mechanical strength without reducing effective surface gain, and herein presents the etching method. Its is characterized by

conducting etching treatment after providing numerous corrosion-resistant fine lines on the aluminum foil surface.

That is, numerous fine lines that resist corrosion and delay the start of erosion are provided on both the front and back face or on either one of the faces of the aluminum foil that undergoes etching treatment. By conducting the etching treatment in this state, a corroded surface is formed that has numerous deep irregularities with a large amount of melting in the parts where the fine lines are not provided, while a corroded surface is formed that has numerous shallow irregularities with hardly any melting or with a small amount of melting in the parts where the fine lines are provided, thereby obtaining etching foil that as a whole possesses superior mechanical strength without impairment of effective surface gain.

There are various methods for providing fine lines that resist corrosion. The simplest method is the printing method. As most printing inks have poor wettability relative to corrosive liquids and serve to delay the advance of corrosion, this method is very effective in implementing the invention of this patent application. In addition, there is also the method that provides oxidized fine lines by heating with laser beams, the method that provides fine lines by the pressing action of a roller, and so on. With the former method, the heat-generated oxides resist corrosion, and with the latter method, the changes in aluminum structure due to the pressure change resist corrosion. These corrosion-resistant fine lines leave high-strength parts in the foil after etching treatment just like a reinforcing foil, with the result that the aluminum foil possesses superior mechanical strength after etching.

The width, spacing and mode of arrangement of the fine lines are selected at one's discretion in relation to the setting of effective surface gain and mechanical strength. Fig. 1

shows the case where numerous fine lines (2) are provided in parallel in the lengthwise direction – that is, the rolling direction – of the aluminum foil (1). With this configuration, tensile strength in the rolling direction and bending strength in the direction orthogonal to the rolling direction are strengthened. Accordingly, as electrode foil that is wound in an ordinary capacitor element is slit cut at the required width in parallel in the rolling direction, this is a most preferable configuration for providing fine lines in the aluminum foil. Fig. 2 shows the case where numerous fine lines (2) are provided in a slanted manner in the aluminum foil (1), while Fig. 3 shows the case where numerous fine lines (2) are provided in the aluminum foil (1) so that they cross in an X-shape. These configurations also result in superior tensile strength and bending strength. Furthermore, Fig. 4 shows a configuration for the case where numerous fine lines (2) are provided in parallel in the direction orthogonal to the rolling direction. This configuration is effective in cutting the aluminum foil (1) to the required width in the direction orthogonal to the rolling direction, and obtaining electrode foil.

Fig. 5 (a) and (b) show enlarged sectional views of the aluminum foil after etching. Fig. 5 (a) shows the case where the fine lines (2) are provided on only one side of the aluminum foil (1), while Fig. 5 (b) shows the case where the fine lines (2) are provided on both sides of the aluminum foil (1).

By providing corrosion-resistant fine lines, it may at first glance appear that the effective surface gain of the aluminum foil will be reduced compared to aluminum foil obtained without providing the fine lines, but experimental results have demonstrated that hardly any difference occurs in the capacity ratio of the capacitor. The reason for this would seem to be that it is sufficient to have the proportion occupied by the fine lines amount to a small percent of the total area, and that the corrosion melt amount that is lost in the fine line parts can be offset by the

other parts without fine lines. Moreover, when the corrosion melt amount of the aluminum in the case where fine lines are provided is identical to that in the case where the fine lines are not provided, the average sectional area of the parts that remain without being corroded becomes approximately equal. Consequently, although it may appear that no difference will occur in mechanical strength, experimental results have demonstrated that a marked difference occurs in mechanical strength. The reason for this would seem to be that the corrosion of the parts where the fine lines are not provided is deep, and these parts are accordingly brittle, tear easily, and their strength per unit of sectional area is low, whereas the fine line parts are tough due to the >*shallow* corrosion, and their strength per unit of sectional area is high.

A detailed description is given in the following embodiments.

Sample 1

Annealed aluminum foil with a thickness of 100 μ and purity of 99.99% was subjected to etching treatment by the conventional electrolytic etching method in a chloride solution, and the solubility loss was controlled to be approximately 38%.

Water rinsing treatment was then conducted, after which formation occured at 375V in a boric acid solution.

Sample 2

With regard to Sample 1, before conducting the etching treatment, fine lines were provided in parallel at intervals of 2.5 mm on one side of the aluminum foil and in the rolling direction of the aluminum foil by marking ink with a width of 0.25 mm.

Sample 3

With regard to Sample 2, the fine lines were provided on both sides.

In these experimental cases, with regard to capacitance measurement, equivalent electrostatic capacity was obtained by conducting measurement by bridge in an electrolytic solution, and this value was then divided by area (cm^2), and the $\mu F/cm^2$ value was calculated. With regard to the measurement of tensile strength, etching foil cut into parallel slits of 10 cm length and 1 cm width in the rolling direction was subjected to tensile force in the rolling direction, the tensile force was increased at the rate of 0.25 kg per second to obtain the kg value at the time of rupture, which was then used to calculate the tensile strength kg/cm value. Furthermore, with regard to bending strength, samples identical to the aforementioned tensile strength measurement samples were bent at a 45° angle in the lengthwise direction with the bent surface at this time being used as the radius of curvature for 1 mm. A tensile force of 250 g was imparted in the lengthwise direction, and the sample was returned from its 45° bent state to its original state, after which it was bent at a 45° angle in the opposite direction, and again returned to its original state, which counted as 1. This procedure was repeated until obtainment of the number of times at which the bent part severed. The results are shown as follows.

Note

	Capacitance $\mu F/cm^2$	Tensile strength Kg/cm	Bending strength
The case of Sample 1	0.72	1.2	3
The case of Sample 2	0.72	1.5	10
The case of Sample 3	0.71	1.8	19

As is clear from the foregoing experimental results, according to this invention, compared to the etching foil obtained by the conventional method, the obtained mechanical strength is very high and there is remarkable improvement in bending strength in particular, despite the fact that capacitance remains approximately the same, and consequently this is clearly very advantageous for the winding operations of the capacitor element in automatic winder devices and for handling operations.

As a result of numerous experiments, as stated above, the method that provides the fine lines by printing is the simplest and most practical. With regard to the printing ink used in this case, it was learned that the full effects are obtainable with either aqueous or oil-based ink. The inventor initially considered that it would be necessary to provide the fine lines on the aluminum foil by thickly applying ink possessing very strong corrosion resistance, but experimental results have shown that the full effects are obtainable even with application of fine lines in a thin layer using ink that is very weak in corrosion resistance. The reason for this would seem to be that corrosion initially progresses in a gradual manner, and subsequently progresses rapidly, and that corrosion in the parts not provided with fine lines has terminated before corrosion has progressed in earnest in the parts provided with fine lines by ink.

4. Brief description of the drawings:

Fig. 1 through Fig. 4 are respectively partial plan views of the etching foil in the embodiments of this invention. Fig. 5 is an enlarged sectional view of the etching foil.

In the drawings, (1) indicates the aluminum foil, and (2) indicates the fine lines.

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Representative:	Patent attorney Shunji Ouchi [seal]

Fig. 1

Fig. 2

Fig. 3

[see source for figures]

Fig. 4

Fig. 5

(a)

(b)

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（全 4 頁）

㊹アルミニウム箔のエッチング方法

㉑特　　願　昭57—192390

㉒出　　願　昭57(1982)11月4日

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明　　細　　書

1. 発明の名称

アルミニウム箔のエッチング方法

2. 特許請求の範囲

(1) アルミニウム箔の表面に腐食に抵抗する多数の細線を施したのち、エッチング処理を行うことを特徴としたアルミニウム箔のエッチング方法。

(2) 細線を、アルミニウム箔の圧延方向に平行して施して成る特許請求の範囲第1項記載のアルミニウム箔のエッチング方法。

(3) 細線を、アルミニウム箔の圧延方向に対し傾斜状に施して成る特許請求の範囲第1項記載のアルミニウム箔のエッチング方法。

(4) 細線を、アルミニウム箔の片面に施して成る特許請求の範囲第1項、第2項または第3項記載のアルミニウム箔のエッチング方法。

(5) 細線を、アルミニウム箔の両面に施して成る特許請求の範囲第1項、第2項または第3項記載のアルミニウム箔のエッチング方法。

3. 発明の詳細な説明

本願は、引張強度並びに折曲げ強度に秀れ、コンデンサ素子の巻取工程における切断などの障害を回避することのできるエッチング箔を得ようとするアルミニウム箔のエッチング方法に関する。

周知のように、電解コンデンサの電極に使用されるアルミニウム箔は、拡面倍率を高めるために表面を腐食するエッチング処理が行われる。

ところでエッチング処理されたのちのアルミニウム箔は引張り強度、折曲げ強度等の機械的強度が腐食によつて低下し、そのためコンデンサ素子を自動巻取装置により巻取る場合などにおいて、端子の取付け部分や巻芯部分で切断する等の不都合な問題があり、エッチング方法の研究者等は如何にして薄いアルミニウム箔に機械的強度を損うことなく大きな拡面倍率が得られるかについて苦心している現状にある。

斯る点に鑑み、本願発明者も種々の研究結果、拡面倍率を低下させることなく機械的強度に秀れたエッチング箔が容易に得られるエッチング方法に成功し、こゝにそのエッチング方法を提案するも

のであり、その特徴とするところは、アルミニウム箔の表面に腐食に抵抗する多数の細線を施したのち、エッチング処理を行うものである。

即ちエッチング処理されるアルミニウム箔の表裏両面或いはそのいづれか一方の面に、腐食に抵抗してその侵食の開始を遅らせる細線を多数施し、この状態でエッチング処理を行うことによつて、細線の施されていない部分に溶解量の大きい深い凹凸を多数有する腐食面を形成すると共に、細線の施された部分には殆んど溶解しないか或いは溶解量の少ない浅い凹凸を多数有する腐食面を形成せしめ、全体として拡面倍率を損うことなく機械的強度に秀れたエッチング箔を得ようとするものである。

腐食に抵抗する細線を施す方法としては種々あるが、最も簡単な方法として印刷法があり、印刷インクの殆んどは腐食液に対するぬれ性が悪く腐食の進行を遅らせるので、この方法が本願発明の実施に極めて有効であり、このほかに、レーザー光線によつて加熱することにより酸化細線を施す方法や、ローラによる加圧作用によつて細線を施す方法などがあり、前者は加熱によつて生じた酸化物が腐食に抵抗し、後者は加圧変化によるアルミニウム組織の変化が腐食に抵抗する。そしてこの腐食に抵抗する細線はエッチング処理後に恰かも補助箔の如き強度の大きい部分をエッチング箔中に残す作用をなし、その結果エッチング後のアルミニウム箔が機械的強度に秀れたものとなるのである。

細線の幅、間隔及び配置の態様等は、拡面倍率及び機械的強度の設定に関連して適宜選択され、第1図はアルミニウム箔(1)の長手方向即ち圧延方向に沿つて多数の細線(2)を平行状に施して成る場合を示しており、この構成によれば、圧延方向における引張強度及び圧延方向と直角方向における折曲げ強度が強くなり従つて通常コンデンサ素子に巻取られる電極箔は、圧延方向に平行して所要幅でスリット切断されるため、アルミニウム箔に細線を施す構成として最も好ましいものである。第2図はアルミニウム箔(1)に多数の細線(2)を斜状に施した場合を、また第3図はアルミニウム箔(1)に多数の細線(2)をX状に交叉するように施した場合を夫々示しており、この構成のものも、引張り強度及び折曲げ強度に秀れた効果を有する。さらにまた第4図は圧延方向と直角方向に多数の細線(2)を平行状に施した場合の構成を示しており、この構成においては、アルミニウム箔(1)を圧延方向と直角方向で所要幅に切断して電極箔を得る場合に有効である。

第5図(イ)及び(ロ)は、エッチング後のアルミニウム箔の拡大断面図を示しており、同図(イ)はアルミニウム箔(1)の片面のみに細線(2)を施した場合を、また同図(ロ)はアルミニウム箔(1)の両面に細線(2)を施した場合を夫々示している。

ところで腐食に対して抵抗する細線を施すことにより、該細線を施さない場合に得られるアルミニウム箔の拡面倍率が一見低下するかの如く感を与えるが、実験の結果によれば、コンデンサ容量比において殆んど差が生じないことが判明した。その理由は、細線部の占める割合が全体の面積の数パーセントで充分であることと、細線部で減じた腐食溶解量が細線のない他の部分で補なうことができることによるものと思料される。また細線を施した場合のアルミニウムの腐食溶解量と、細線を施さない場合のそれとが同一であるとするとき、腐食されずに残つた部分の平均断面積は略ゞ等しくなるので、機械的強度にも差が生じないかの如き感を与えるが、実験の結果によれば、機械的強度に著しい差が生じることが判明した。その理由は、細線が施されていない部分の腐食は深く、従つて該部分は脆弱で裂け易く、単位断面積あたりの強度が小さいのに対し、細線部においては、腐食が浅いため強靭で、単位断面積あたりの強度が大きいためであると思料される。

次に実施例について詳述する。

試料1

厚さ100μ、純度99.99%、焼鈍ずみのアルミニウム箔を塩化物溶液中で慣用されている電解エッチング法によりエッチング処理を行い、かつ溶解減量を約38%となるように制御

し、次いで水洗処理したのち、硼酸液中で375Vにおいて化成したもの

試料2

試料1において、エッチング処理を行う前に2.5㎜間隔で、0.25㎜幅のマジックインクにより細線をアルミニウム箔の圧延方向に平行にかつその片面に施したもの

試料3

試料2において、細線を両面に施したもの

本実験例において、容量測定は、電解液中で電橋による測定を行つて等価直列静電容量を求め、その値を面積（㎠）で除して$\mu F/cm^2$値を算出した。また引張り強度の測定は、圧延方向に平行に長さ10㎝、幅1㎝にスリット切断したエッチング箔に対し圧延方向に引張り力を与え、毎秒0.25Kgの割合で引張り力を増加して破断時のKg値を求め、その引張り強度Kg/cm値を算出した。更に折曲げ強度については、上記した引張り強度測定試料と等しい試料をその長さ方向に対し45度角に曲げ、このときの曲げの面は1㎜の曲率半径とし、長さ方向に引張り力250g加え、かつ曲げ方は、始め45度角に曲げた状態から元に戻どし、次いで反対方向に45度角曲げ、再び元に戻す操作を1回とし、その折曲部が切断するまでの回数を求めた。その結果下記の通りである。

記

	容量$\mu F/cm^2$	引張り強度Kg/cm	折曲げ強度
試料1の場合	0.72	1.2	3
試料2の場合	0.72	1.5	10
試料3の場合	0.71	1.8	19

上記した実験結果から明らかなように、本願発明によれば、従来方法によるエッチング箔と比較して容量が略々同一であるにも不拘、得られる機械的強度は非常に大きく、特に折曲げ強度の改善が著しいため自動巻取機によるコンデンサ素子の巻取り作業並びに取扱い作業に極めて有利であることが理解される。

なお数次にわたる実験の結果によれば、さきに述べたように印刷によつて細線を施す方法が最も簡単で実用的であり、この場合に用いられる印刷インクは、水性でも油性でも充分な効果が得られることを知得した。発明者は当初極めて強い耐腐食性のインクで、かつ厚く塗布してアルミニウム箔に細線を施す必要があるものと思慮していたが、実験の結果によれば、耐腐食性の極めて弱いインクで、かつ薄い層の細線でも充分な効果が得られた。それは腐食の進行がその当初では緩徐で、その後において急速に進行するものであり、インクによつて施された細線部が本格的に腐食進行する以前に、細線を施さない部分の腐食が終了してしまうためであると思料される。

4. 図面の簡単な説明

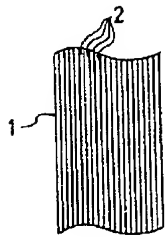
第1図乃至第4図は夫々本願発明の実施例におけるエッチング箔の部分平面図、第5図はエッチング箔の拡大断面図である。

図中(1)はアルミニウム箔、(2)は細線である。

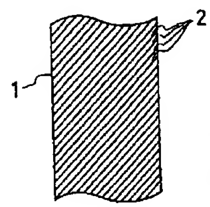
特許出願人　日本蓄電器工業株式会社

代理人弁理士　大内俊治

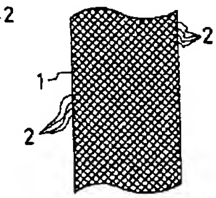
第 1 図



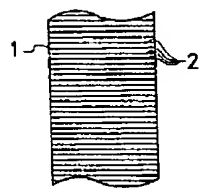
第 2 図



第 3 図



第 4 図



第 5 図